De-perturbative corrections for charge-stabilized double ionization potential equation-of-motion coupled-cluster method

Tomasz Kuś and Anna I. Krylov

Additional information on J. Chem. Phys.

De-perturbative corrections for charge-stabilized double ionization potential equation-of-motion coupled-cluster method

Tomasz Kuś and Anna I. Krylov

Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482, USA

Charge stabilization improves the numeric performance of double ionization potential equation-of-motion (EOM-DIP) method when using unstable (autoionizing) dianion references. However, the stabilization potential introduces an undesirable perturbation to the target states' energies. Here we introduce and benchmark two approaches for removing the perturbation caused by the stabilization. The benchmark calculations of excitation energies in selected diradicals illustrate that the so-called core correction based on evaluating the perturbation in a small basis set is robust and yields reliable EOM-DIP values, i.e., the errors of 0.0–0.3 eV against a similar-level coupled-cluster approach. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4730296]

I. INTRODUCTION

The double ionization potential equation-of-motion (EOM-DIP) method[1–3] is a non-particle-conserving member of the EOM coupled-cluster (EOM-CC) family[4–7] targeting diradicals and other problematic multi-configurational wave functions. In EOM-CC, target states, $\Psi_k = R_k \Phi_0$, are found as the solutions of a non-Hermitian eigenvalue problem:

$$\bar{H} R_k = E_k R_k, \tag{1}$$

where

$$\bar{H} = e^{-T} H e^{T} \tag{2}$$

is a similarity transformed Hamiltonian; T is a general excitation operator of the following form:

$$T = \sum_{ia} t_i^a a^\dagger i + \sum_{i<j} \sum_{a<b} t_{ij}^{ab} a^\dagger b^\dagger j i + \cdots$$
$$+ \sum_{i<j<\cdots<k} \sum_{a<b<\cdots<c} t_{ij\cdots k}^{ab\cdots c} a^\dagger b^\dagger \cdots c^\dagger k \cdots j i. \tag{3}$$

We follow the standard second-quantization notation in which a, b, ... denote virtual spin-orbitals, whereas i, j, ... denote occupied spin-orbital indices (with respect to the reference determinant, Φ_0). The T amplitudes are determined from the CC equations for the reference state (Φ_0).

The choice of the excitation operator R is specific for different EOM-CC models,[4] e.g., it is a particle-conserving operator in EOM-EE (EOM for excitation energies),[8] a particle-annihilating operator in EOM-IP (EOM ionization potential),[9] a particle-creating operator in EOM-EA (electron attachment EOM),[10] and a spin-flipping (SF) operator in EOM-SF.[11–13] The EOM-DIP models employ R that removes two occupied (with respect to Φ_0) spin-orbitals from each determinant (hence, DIP).

The excitation level in T and R defines a particular EOM-CC model and determines its accuracy and computational cost. Our study employs EOM-CC methods that use operators restricted to the single and double substitutions (with respect to the reference Φ_0), that is, $1h1p + 2h2p$ (h for hole, p for

particle) in T (and in R in particle-conserving EOM models), whereas the respective excitation level of R in EOM-DIP is $2h + 3h1p$. Thus, amplitudes T for these models are found from the CCSD (coupled-cluster with single and double substitutions) calculations for the reference state.

Similar to EOM-SF, the EOM-DIP method can describe electronic structure in the cases when the standard coupled-cluster and spin-conserving EOM (EOM-EE) methods suffer from an unbalanced treatment of near-degenerate configurations,[4] such as diradicals and bond-breaking. Compared to the SF method, EOM-DIP can tackle more extensive degeneracies, such as 4-electrons-in-3-orbitals, which are encountered in oxygen-containing diradicals, e.g., adducts of oxygen to unsaturated hydrocarbons.[14–17] However, despite its potential, practical applications of EOM-DIP have been limited[2,3,18] owing to unstable (autoionizing) character of doubly charged anions that need to be employed as references to describe neutral diradical states in the EOM-DIP formalism.

Nooijen and co-workers[19,20] have addressed this issue by devising a composite state-specific scheme in which the similarity-transformed Hamiltonian is constructed for each state separately by solving modified coupled-cluster equations for a particular multi-configurational reference obtained from a separate multi-reference calculation, e.g., complete active space self-consistent field. The authors have been able to overcome numeric difficulties due to nearly singular nonlinear amplitude equations and reported encouraging results for several diradical systems[21,22] and bond-breaking.[20] However, the state-specific nature of this approach complicates the calculations of multiple electronic states and, especially, interstate properties such as transition dipole moments and nonadiabatic couplings.

Our goal is to retain a multi-state nature of EOM-DIP and to remain in a strictly single-reference domain as far as formalism is concerned (just as other EOM-CC models,[4] EOM-DIP is a single-reference method capable of describing multi-configurational wave functions). To improve the performance of EOM-DIP, we recently investigated a computational

136, 244109-1

strategy of stabilizing these unstable references by an additional Coulomb potential,[23] exploiting the ideas developed in the context of metastable (with respect to electron detachment) states, i.e., so called resonances.[24,25] Such positive potential increases the electron-detachment energy and pushes the electron-detached (continuum) states up, such that the dianion state becomes the lowest state of the system. Thus, it effectively separates the dianionic ground state from the continuum states. When the gap between the dianion state the continuum becomes sufficiently large, the doubly attached and the continuum states do not mix, and the dianion state becomes a good reference state for the DIP expansion.

The specific choice of the form of the potential and its strength is somewhat arbitrary. A common sense requires that the potential is strong enough to stabilize the system, but not too strong to significantly perturb the target wave functions.[26,27]

In the previous paper,[23] we considered two forms of the stabilizing potential that have been employed in the context of metastable negatively charged species. The first one is a spherical potential embedding a molecule (the potential can be represented either approximately, by point charges, or analytically, by an exact spherical potential).[26–30] We will refer to this approach as the charged cage method. In the second approach, the nuclear charge variation (NCV) method, the stabilizing potential is produced by scaling the charge of each nucleus by a certain value.[31] Below, we consider both approaches and discuss their advantages and limitations.

Unfortunately (although not unexpected), the additional potential perturbs the target states causing errors whose magnitude depends on the strength of the potential and its shape relative to molecular shape. This problem has been recognized and several solutions have been proposed.[26,27,30,31]

In the previous paper,[23] we focused on choosing the optimal strength of the potential. Here, we introduce two variants of a correction aiming at reducing the errors due to the stabilizing potential, i.e., a perturbative correction and a core correction.

The perturbative correction is based on the perturbative treatment of the Hamiltonian. Following the standard presentation of the perturbation theory (PT),[32] we divide the total Hamiltonian of the system into the perturbation part (V) and a zero-order part (H_0) for which the solutions of the Schrödinger equation are known:

$$H = H_0 + V. \tag{4}$$

For our purposes, we choose H_0 to be the full Born-Oppenheimer Hamiltonian of the molecule *plus* the additional Coulomb potential. Thus, in order to recover solutions for the unstabilized molecular Hamiltonian, V must be a negative of the Coulomb interaction operator:

$$V \equiv V^{pot} = \sum_i^{N_{el}} \sum_m^{N_{ch}} \frac{Q_m}{|\mathbf{r_i} - \mathbf{r_m}|}, \tag{5}$$

where Q_m and $\mathbf{r_m}$ are the value of the charge and position vector, respectively, of the mth point charge used to generate the stabilizing potential, and $\mathbf{r_i}$ is the position vector of the ith electron. Having defined the perturbation operator, we arrive

at the first order PT correction to the energy, Δ^p:

$$\Delta_k^p = \langle \Psi_k | V^{pot} | \Psi_k \rangle = Tr[\rho_k \mathbf{V^{pot}}], \tag{6}$$

where Ψ_k is the DIP target state wavefunction and ρ_k is the corresponding one-particle density matrix. Thus, the corrected energy of the kth DIP state is: $E_k^p = E_k + \Delta_k^p$. Since one needs only the one-particle EOM density matrix to compute the correction, the cost of the perturbative correction is a small fraction of the total cost of the calculation. Note that the correction is state-specific and should be computed for each target doubly ionized state. This form of the correction was inspired by the perturbative correction introduced by Slipchenko to account for the polarization response of a solvent environment to electronic excitation of a solute.[33]

The second correction, called the core correction, is based on the assumption that the perturbation of the target states by the stabilizing potential is not basis set dependent and, therefore, can be computed in a relatively small basis set in which the dianionic states are artificially stabilized by a compact (non-diffuse) basis that consists only of "core" functions. This leads to a simple scheme in which the correction, Δ_k^c, is computed for each state k as the total energy difference between the two calculations in a small basis set, without and with the stabilizing potential:

$$\Delta_k^c = E_k^0 - E_k^{st}, \tag{7}$$

where E_k^0 and E_k^{st} are the total DIP energies of the target state k computed without and with the stabilizing potential, respectively, using a small basis set. The corrected DIP energy of the target state k, E_k^c, is obtained by adding the correction to the total state's energy, E_k, obtained in the stabilized calculation using the target (large) basis set: $E_k^c = E_k + \Delta_k^c$.

The choice of the small basis set for the correction calculation (referred to as a calibration basis) is not uniquely defined. Our tests indicate that the best accuracy is achieved when the basis set used for calibration is a subset of the target basis set, such that it does not contain higher angular momentum functions and functions with smaller exponents. For example, if the target basis set is 6-311(2+,2+)G(3*df*,3*pd*),[34] a good choice of the calibration basis is 6-311G(*d*,*p*).[35] Likewise, cc-pVDZ (Ref. 36) serves as a good calibration basis for the aug-cc-pVTZ[37] calculations. As illustrated by the numerical examples below, despite its simplicity, the core correction performs very well.

In Sec. II, we outline our benchmark strategy and computational details. We then present the results and discussion. Our concluding remarks are given in Sec. III.

II. BENCHMARK CALCULATIONS

We benchmark the performance of the corrections using selected diradicals (CH_2, NH_2^+, SiH_2) and cyclobutadiene. We also consider ground and excited states of NO^- that have autoionizing character.

We focus on the EOM-DIP model with single and double substitutions in the CC part and $2h$ and $3h1p$ excitations in the EOM part (EOM-DIP-CCSD, which is sometimes regarded as a mixed CCSD/CCSDT variant of the EOM-DIP method). For diradicals (CH_2, NH_2^+, SiH_2) and NO^-, we benchmark

the EOM-DIP-CCSD against EOM-SF-CCSD. Since we use only the EOM-DIP-CCSD and EOM-SF-CCSD methods in the study, we abbreviate the two models as DIP and SF, respectively.

A. Computational details

The calculations illustrating the dependence of the errors in DIP excitation energies in diradicals and NO^- on the strength of stabilization potential are carried out using the 6-311(2+,2+)G(3df,3pd) basis set. The core correction in these DIP calculations is computed using 6-311G(d,p).

The cyclobutadiene calculations are performed with the aug-cc-pVDZ and cc-pVTZ bases,[37] and the cc-pVDZ basis is used to compute the core correction.

The accuracy of all DIP calculations is assessed with respect to the SF results at the same geometry and with the same basis set.

In the charged cage stabilization method, we use a spherical distribution of a large number of identical point charges, which effectively simulates the spherical cage located in the molecular center of mass (i.e., the potential which would be generated by such cage). Although for most cases, a dodecahedral cage is sufficient in terms of accuracy, we use much more dense and uniform distribution of point charges to ensure that even for small radii the errors caused by using point charges instead of the analytical potential are small.

Vertical and adiabatic excitation energies of CH_2, NH_2^+, and SiH_2 are calculated at the same geometries as in Ref. 38 and in our previous paper.[23] Cyclobutadiene calculations are performed using the geometries computed at the CCSD(T)/cc-pVTZ level of theory.[12] Calculations of NO^- are performed for the internuclear distance of 2.1747 a.u. In all calculations, all electrons are correlated.

The calculations were performed using the *Q-CHEM* electronic structure package.[39]

B. Excitation energies in selected diradicals

We begin by considering vertical excitation energies of the three benchmark systems, with an aim to establish a relation between the strength of stabilization potential and the accuracy of the DIP method for the charged cage and NCV methods. We vary the potential by changing the stabilization parameters in the range of 3.0–1.5 Å (sphere radius in the charged sphere method) and 0.6–2.5 a.u. (additional charge in the NCV method). For the charged cage method, we use the total charge of +10 a.u. for CH_2 and SiH_2, and +5 a.u. for NH_2^+; such values of the total charge yield the shape of stabilization curves that allows us to unambiguously retrieve excitation energies. The details of the procedure used to determine the excitation energies from the stabilization plots are given below.

A difficulty one faces when applying the stabilization methods is a relatively strong dependence of the excitation energy on stabilization parameters, which ultimately affects the accuracy and utility of the stabilized DIP calculations.[23] A robust correction should mitigate this dependence resulting in more constant stabilization curves (energy versus the strength of the potential), or, at least, curves exhibiting plateaus in a relatively broad range of parameters, such that excitation energies can be unambiguously determined as values at the plateaus (or broad extrema) of the stabilization curves.

In the present study, we consider a broader range of the stabilization potentials than in the previous study, including very strong potentials that might seem unphysical. However, calculations with such strong potentials allow us to gain an insight in the stabilization process. For example, we found that in order to reach a nearly constant dependence of the (corrected) excitation energy on the stabilization potential, one must employ strong potentials. In some cases the required potential is so strong that it cannot be generated by the charged cage because the required cage is so small that it approaches the atoms. For such cases, one needs to employ the NCV method that can generate arbitrary strong potentials.

As explained above, ideally, the excitation energy in stabilized calculations should be determined as a value of a plateau (or a broad extremum) of the stabilization curve. In most cases that we analyzed, this is readily visible. To illustrate this point, consider Figs. 1–6 that present vertical excitation energies plotted as a function of the stabilization potential. As one can see, the uncorrected stabilized DIP values depend strongly on the stabilization potential. Disappointingly, the perturbative correction, although it reduces the magnitude of the error, does not lead to the curves with a plateau, even for a narrow range of the potential. In contrast, the core correction curves exhibit extended plateaus particularly prominent for the NCV method, or relatively broad extrema in the case of the charged cage method. Another advantage of the core correction is that the core-corrected DIP values obtained by the charged cage and NCV methods are within 0.08 eV from each other, except one case (SiH_2, $2\,^1A_1$ state, discrepancy of about 0.15 eV). Such good agreement indicates that the core correction is robust and allows one to remove errors caused by the stabilization potential from DIP excitation energies. We note that the errors of the core-corrected DIP method against SF never exceed 0.28 eV (for most cases less than 0.1 eV), which is consistent with expectations based on a comparison of DIP and SF results for well-behaved (i.e., stable) systems.[23]

Let us now compare the two stabilization approaches using the core correction. It is clear that the curves for the NCV method exhibit more reliable behavior, converging almost smoothly to a certain value in most cases. At the same time, the curves calculated with the perturbatively corrected NCV method change linearly in the entire range of potential, with relatively large errors that reach up to a few eV for some cases.

In the light of the above analysis, some conclusions from Ref. 23 should be revisited. One important finding that emerges from the calculations of the corrected stabilized DIP values is that unexpectedly large potentials are required to fully stabilize an unstable system. This of course perturbs the target states to a larger extent, but, as we demonstrate, these errors are reduced by the corrections, especially efficiently in the case of the core correction. Hence, although the procedure of finding the optimal stabilization parameters described in Ref. 23 is correct and robust, the strategy proposed here is more accurate and easily applicable in a black-box fashion. Also, we want to clarify that what we previously attributed to
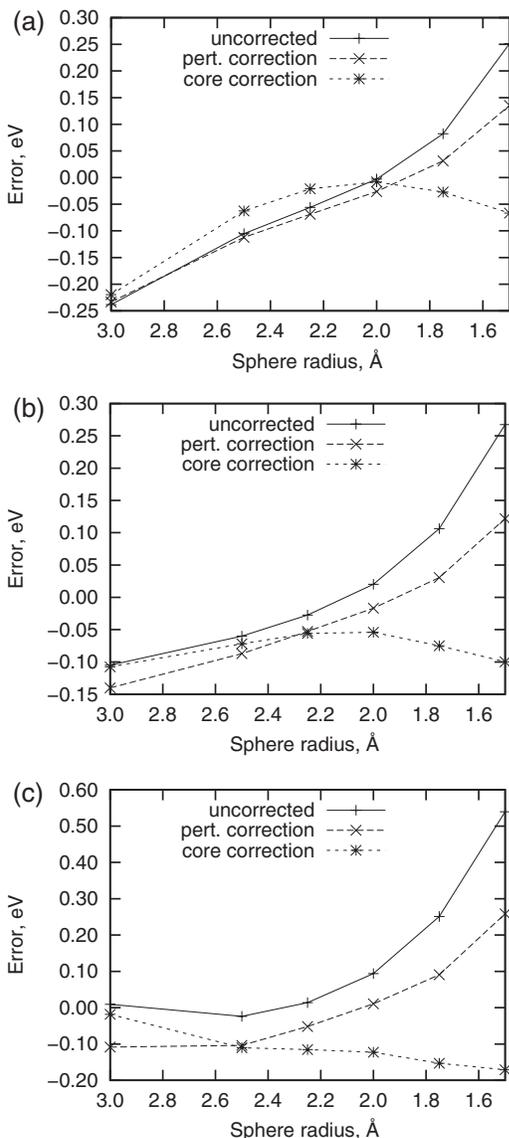
FIG. 1. DIP errors against the SF values for the vertical excitation energies of the three lowest states of methylene using the charged cage of +10 a.u. The plots show the errors of stabilized DIP for uncorrected, perturbatively corrected, and core-corrected calculations. For the core correction approach, the DIP errors and stabilization parameters corresponding to the optimal DIP accuracy (see text for details) are −0.11 eV/2.0 Å, −0.05 eV/2.0 Å, and −0.11 eV/2.5 Å for the three states, respectively.
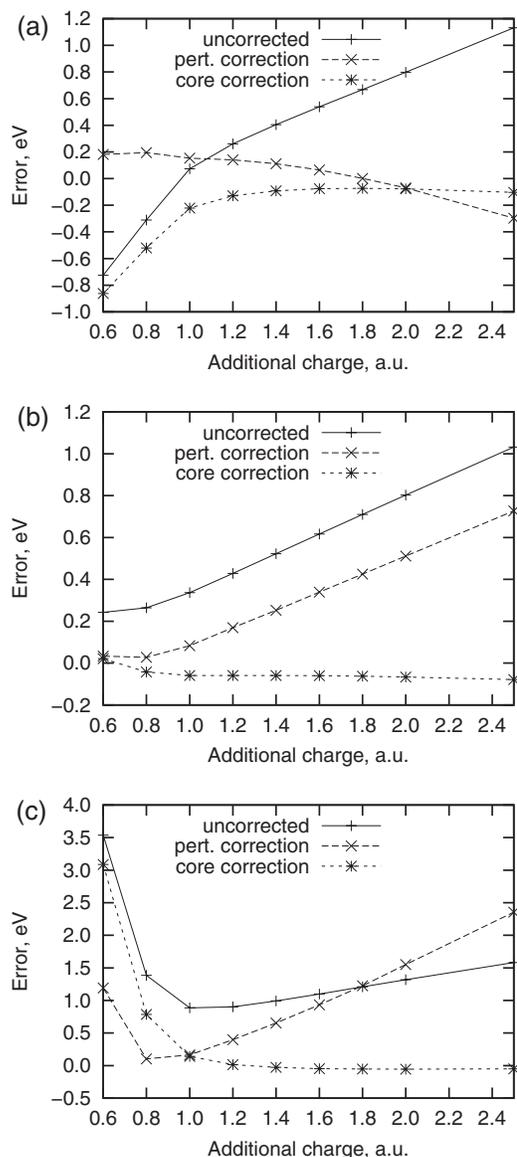

FIG. 2. DIP errors against the SF values for the vertical excitation energies of the three lowest states of methylene using the NCV approach. The plots show the errors of stabilized DIP for uncorrected, perturbatively corrected, and core-corrected calculations. For the core correction approach, the DIP errors and stabilization parameters corresponding to the optimal DIP accuracy (see text for details) are −0.07 eV/1.8 a.u., −0.08 eV/2.5 a.u., and −0.03 eV/1.4 a.u. for the three states, respectively.

a potential-induced errors were in fact discrepancies resulting from insufficient stabilization.

Next, we present stabilization plots obtained in calculations of adiabatic excitation energies (Figs. 7–9) focusing on the singlet-triplet (ST) gaps in the selected diradicals. Since the adiabatic energy difference requires two separate calculations, the error cancellation is significantly reduced, which makes these tests more demanding. Indeed, the variation of uncorrected DIP errors is considerably larger than in the vertical excitation energy calculations. Similarly, the perturbatively corrected adiabatic excitation energies show larger errors. However, the quality of the core correction remains the same as in the vertical excitation calculations. The excitation energies computed with the charged cage and NCV methods are similar, differing by absolute values of 0.10, 0.01, and

0.03 eV for CH_2, NH_2^+, and SiH_2, respectively. We note that using stabilization potentials in calculations of potential energy surfaces (PESs) requires caution. We expect that using NCV stabilization in which additional charges move with the atoms is better suited for calculations of PESs than charged cage stabilization in which the stabilizing potential remains fixed.

Let us now discuss the NH_2^+ results in more detail. NH_2^+ is distinct from the other two systems because it is stable in the context of DIP calculations, i.e., at the HF/6-311(2+,2+)G(3df,3pd) level, the ground state of NH_2^- lies 0.27 hartree below the ground state of NH_2^+. This means that in the stabilized DIP calculations, one stabilizes a system which is already stable with respect to electron
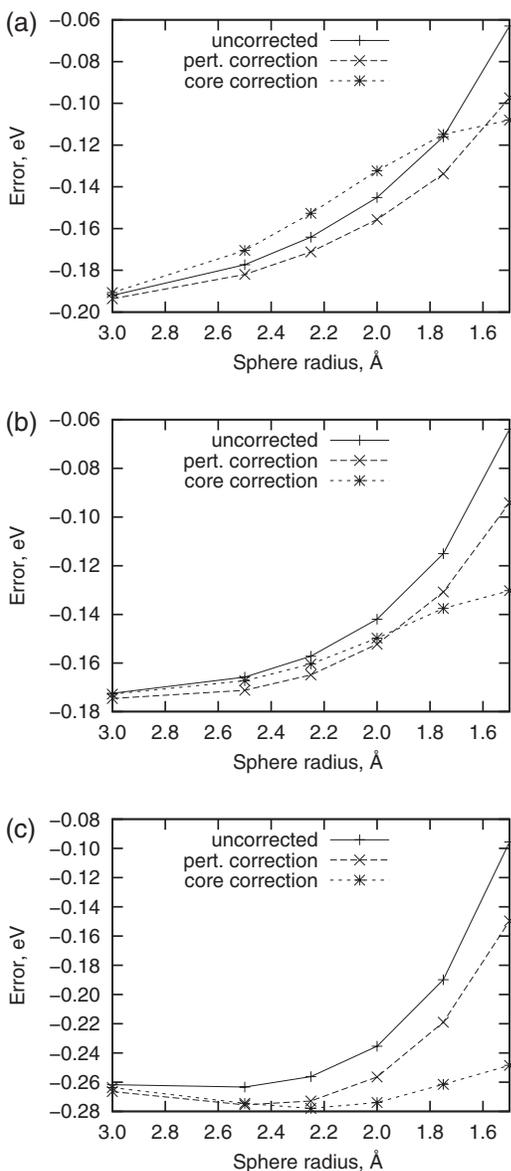
FIG. 3. DIP errors against the SF method for the vertical excitation energies of the 3 lowest states of NH_2^+ using the charged cage of +5 a.u. The plots show the errors of stabilized DIP for uncorrected, perturbatively corrected, and core-corrected calculations. For the core correction approach, the DIP errors and stabilization parameters corresponding to the optimal DIP accuracy (see text for details) are −0.11 eV/1.5 Å, −0.13 eV/1.5 Å, and 0.28 eV/2.25 Å for the three states, respectively.

FIG. 4. DIP errors against the SF values for the vertical excitation energies of the three lowest states of NH_2^+ using the NCV approach. The plots show the errors of stabilized DIP for uncorrected, perturbatively corrected, and core-corrected calculations. For the core correction approach, the DIP errors and stabilization parameters corresponding to the optimal DIP accuracy (see text for details) are −0.11 eV/1.4 a.u., −0.13 eV/1.6 a.u., and −0.22 eV/2.5 a.u. for the three states, respectively.

detachment. Hence, the DIP calculations are free of errors that might result from an insufficient stabilization and allow us to focus on the errors caused by the potential. As expected, the DIP accuracy of NH_2^+ results changes less as the stabilization progresses than in the other two molecules, but is still significantly large for the NCV method. However, the core-corrected results are highly consistent between the charged cage and NCV DIP results (discrepancies of 0.00, 0.00, and 0.06 eV for the three states). Also, the unstabilized DIP errors are in the acceptable range (−0.11, −0.13, and −0.22/−0.28 eV). These observations further illustrate the robustness of the core correction.

Summarizing the results presented so far, we conclude that the corrections facilitate determining the optimal stabi-
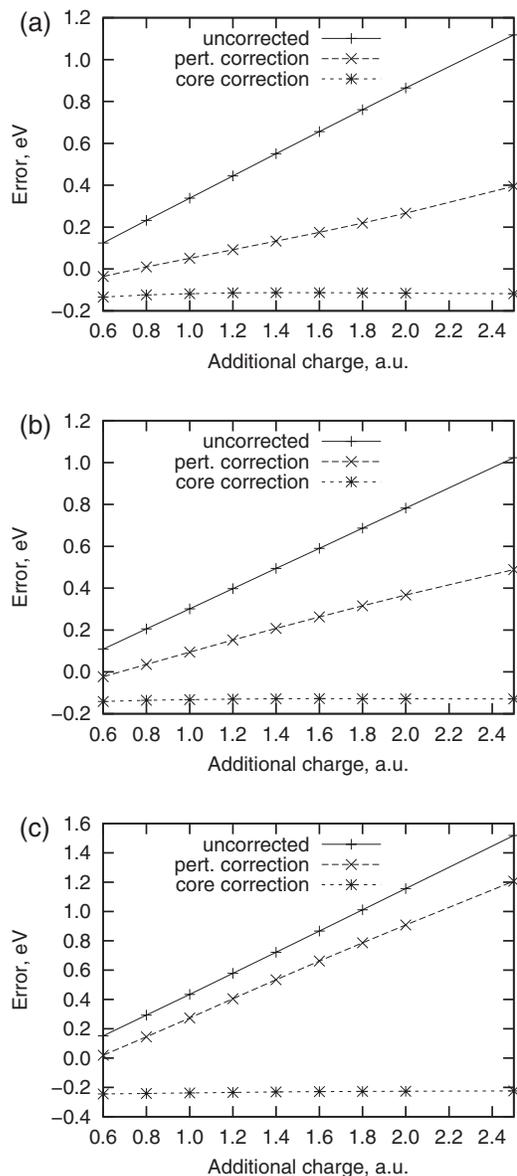
lization parameters, and thus, improve the accuracy of the stabilized DIP calculations. The core correction yields more accurate results, especially when combined with the NCV method. The combination of the NCV method and core correction allows us to reduce the DIP errors (versus SF) below 0.28 eV, usually of about 0.1 eV or better. This is a similar span of accuracy as for the DIP calculations involving stable species (i.e., such systems for which in a given basis set the dianion energy is lower than the one of the neutral system).

Since the core-corrected NCV method produces the most accurate results, in Sec. II C we verify whether such good accuracy is transferable to larger systems.
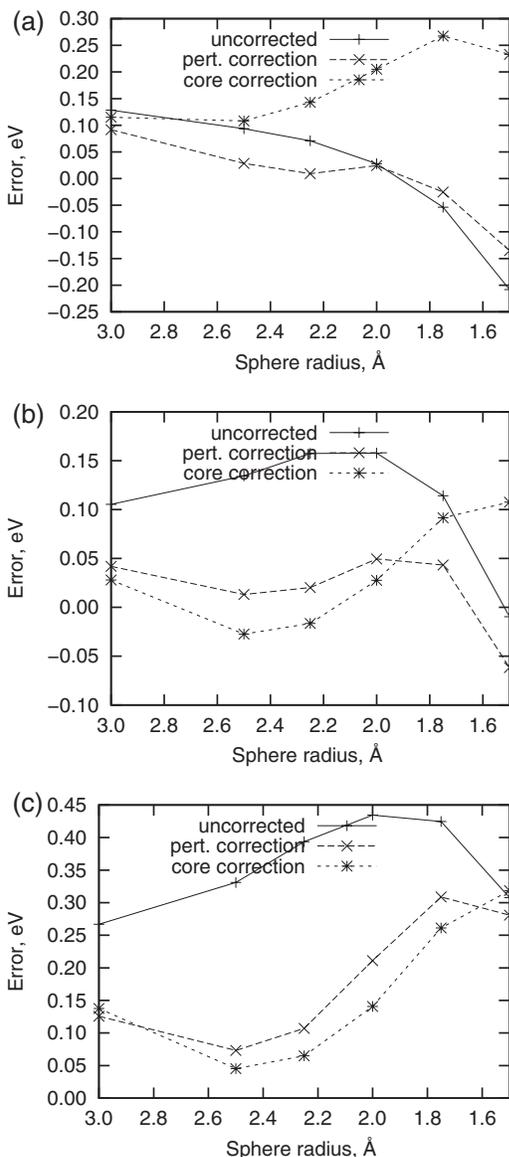
FIG. 5. DIP errors against the SF values for the vertical excitation energies of the three lowest states of SiH$_2$ using the charged cage of +10 a.u. The plots show the errors of stabilized DIP for uncorrected, perturbatively corrected, and core-corrected calculations. For the core correction approach, the DIP errors and stabilization parameters corresponding to the optimal DIP accuracy (see text for details) are 0.11 eV/2.5 Å, −0.03 eV/2.5 Å, and 0.05 eV/2.5 Å for the three states, respectively.

FIG. 6. DIP errors against the SF values for the vertical excitation energies of the 3 lowest states of SiH$_2$ using the NCV method. The plots show the errors of stabilized DIP for uncorrected, perturbatively corrected, and core-corrected calculations. For the core correction approach, the DIP errors and stabilization parameters corresponding to the optimal DIP accuracy (see text for details) are 0.10 eV/1.8 a.u., 0.08 eV/1.6 a.u., and 0.21 eV/1.6 a.u. for the three states, respectively.

C. Cyclobutadiene

Cyclobutadiene is an excellent benchmark system[12,40–64] owing to the following two features. First, cyclobutadiene poses difficulties for standard single-reference methods, especially at the square geometry at which the HOMO and the LUMO are degenerate and the ground state wave function has a two-configurational character.[12,40–42] Second, the cyclobutadiene dianion is metastable and requires stabilization when employing the DIP method.[23]

Here we focus on the comparison of the vertical excitation energies against SF for the two isomers of cyclobutadiene, as well as on the adiabatic energy barrier for the inter-conversion between the two isomers. For comparison purposes, we use data from Ref. 12, calculated with the cc-
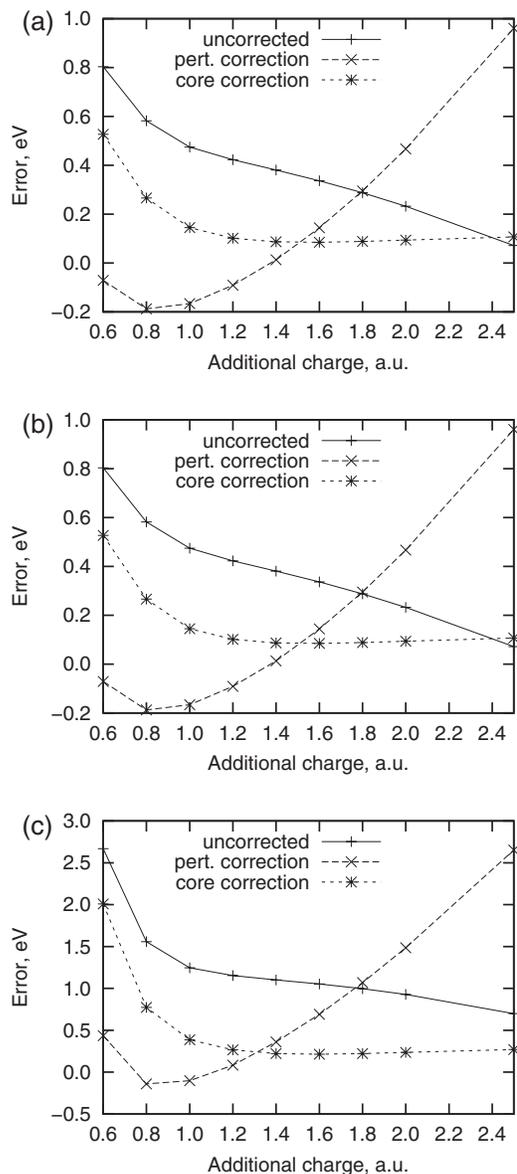
pVTZ basis set. Since cc-pVTZ is not sufficiently diffuse to fully reveal the destabilization of the dianion state, we calculate additional SF results in the aug-cc-pVDZ basis set and use them to benchmark the stabilized DIP technique. We use the cc-pVDZ basis to compute the core correction, because cc-pVDZ is similar to the target basis and is not too diffuse. The results are collected in Table I. For each isomer the two lowest vertical excitation energies are computed. In addition, the isomerization barrier is determined and compared with the SF results. The results confirm the conclusions drawn from the analysis of vertical excitation energies of the three small diradicals, with the caveat that the differences between DIP and SF are somewhat larger for cyclobutadiene (but never

TABLE I. Excitation energies (eV) computed by the DIP method stabilized with NCV of 1.8 a.u. of additional charge and improved by the core correction. SF denotes the EOM-SF-CCSD value computed without the stabilization potential and in the same basis set. Vertical excitation energies are computed with respect to the X^1A_g and X^1B_{1g} states for the rectangular and square forms, respectively.

	Rectangular		Square		
	$1\,^3B_{1g}$	$2\,^1B_{1g}$	$1\,^3A_{2g}$	$2\,^1A_{1g}$	$X^1A_g \rightarrow X^1B_{1g}$
SF/cc-pVTZ	1.659	3.420	0.369	1.824	0.325
DIP/cc-pVTZ	1.577	3.201	0.082	1.474	0.566
SF/aug-pVDZ	1.626	3.404	0.375	1.798	0.279
DIP/aug-pVDZ	1.620	3.343	0.124	1.544	0.450

exceeding 0.3 eV). A small increase in discrepancies between DIP and SF seems to be unrelated to the stabilization procedure, as the differences are larger in the less diffuse basis.

D. Ground and excited states of NO⁻

The next example we consider is NO⁻. For this system, we investigate the performance of the stabilization techniques not only for DIP, but for other CC approaches as well. The results are presented in Table II. We consider the three lowest states of NO⁻: $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^-$. These states arise from distributing two electrons over two (near)-degenerate orbitals
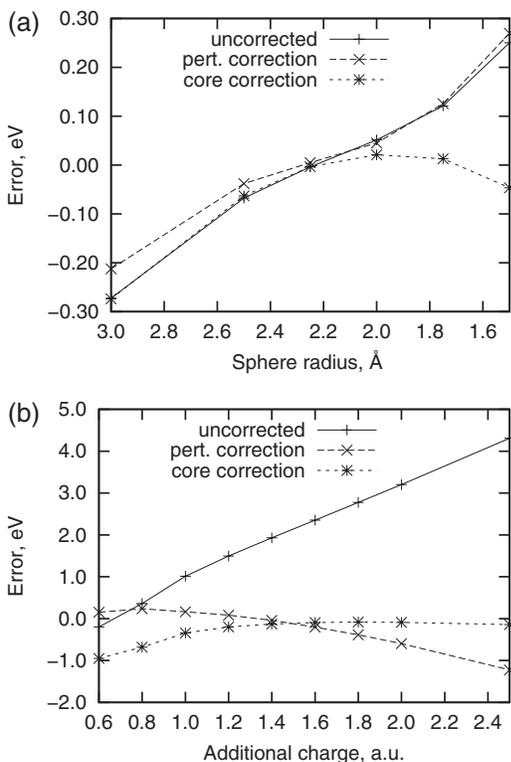

FIG. 7. DIP errors against the SF values for the adiabatic excitation energy of the ST gap of CH₂ using the charged cage of +10 a.u. and NCV approaches, respectively. The plots show the errors of stabilized DIP for uncorrected, perturbatively corrected, and core-corrected calculations. For the core correction approach, the DIP errors and stabilization parameters corresponding to the optimal DIP accuracy (see text for details) are 0.02 eV/2.0 Å, and −0.08 eV/1.8 a.u. for the two stabilization methods, respectively.
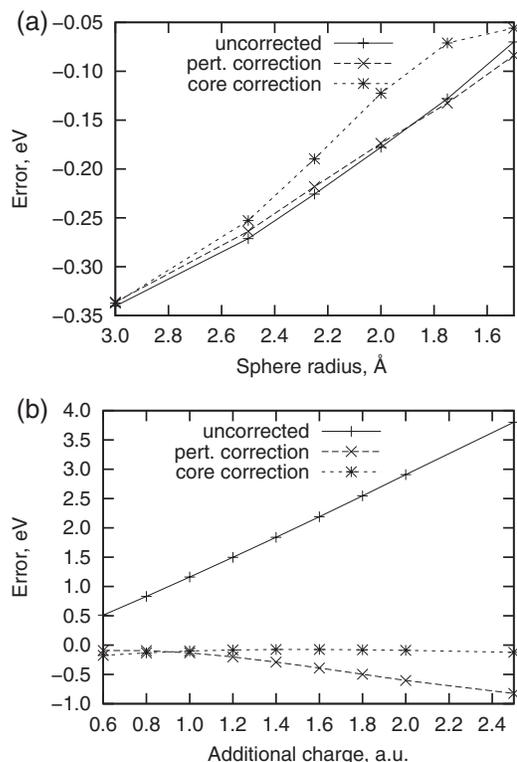

FIG. 8. DIP errors against the SF values for the adiabatic excitation energy of the ST gap of NH_2^+ using the charged cage of +5 a.u. and NCV approaches, respectively. The plots show the errors of stabilized DIP for uncorrected, perturbatively corrected, and core-corrected calculations. For the core correction approach, the DIP errors and stabilization parameters corresponding to the optimal DIP accuracy (see text for details) are −0.06 eV/1.5 Å, and −0.07 eV/1.6 a.u. for the two stabilization methods, respectively.

$(2\pi^2)$, which is similar to a diradical pattern. Thus, from the EOM-CC perspective, only the SF and DIP methods are appropriate for this type of electronic structure.[11]

These three states have been studied theoretically[65–70] as a part of investigating electron-NO scattering processes in the collision energy region below 3 eV. A study of potential energy surfaces of the three states of NO⁻ indicates that at the equilibrium geometry of 2.1747 a.u., all three states are located above the ground state of NO.[69] Thus, it is difficult to calculate the energies of such states using a variational method. Since this is a situation that requires stabilization, we further verify the core-corrected NCV method by computing resonance energies of NO⁻ at the equilibrium geometry and comparing them with the available theoretical data. This is a challenging test for stabilized DIP calculations because the reference function in such case is a triple anion, which presumably has even more unstable character.

In the NO⁻ calculations, we employ a variety of CC-based techniques to determine resonance energies of the $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^-$ states. Computing relative energies of the $^1\Delta$ and $^1\Sigma^-$ states with respect to the $^3\Sigma^-$ state is straightforward for the SF and DIP methods, and the standard methodology is used (the $^3\Sigma^-$ state of NO⁻ becomes the reference function in SF calculations, and the ground state of NO⁻³ is the reference in the DIP calculations).

It is more difficult to determine the energy gap between the ground states of NO and NO⁻. A reasonable choice for

TABLE II. Energy differences between electronic states of NO^- (eV) at the equilibrium geometry (2.1747 bohr) computed with different approaches. All EOM methods use stabilization generated by the nuclear charge variation (1.8 a.u. of the total charge) and corrected by the core correction computed with 6-311G(d,p). The 6-311(2+,2+)G(3df,3pd) basis set is used in all CC, EOM-CC, and EOM-DIP calculations.

States	CC, EOM-CC	EOM-DIP	Ref. 69[a]	Ref. 66	Ref. 67	Ref. 69[b]
$^3\Sigma^- \to {}^2\Pi_g$	1.55[c], 1.48[d], 0.43[e]	...	0.44	0.46	0.90	0.46
$^1\Delta \to {}^3\Sigma^-$	0.90	0.91	0.79	0.68	0.90	1.09
$^1\Sigma^+ \to {}^3\Sigma^-$	1.63	1.62	1.63	...	1.77	...

[a]Complex Kohn method.
[b]Analytic continuation method based on CCSD(T) calculations.
[c]EOM-IP-CCSD calculations.
[d]EOM-EA-CCSD calculations.
[e]Energy difference between core-corrected CCSD(T) for the triplet state and unstabilized CCSD(T) for the doublet state.

such calculations seems to compute the $^2\Pi \to {}^1\Delta$ energy gap using the EOM-IP-CCSD scheme with the $^1\Delta$ state of NO^- as the reference. However, since the $^1\Delta$ state is not well described by CCSD owing to its diradical character, we consider another strategy to be more reliable, i.e., using the $^3\Sigma^-$ state of NO^- as the reference in the EOM-IP-CCSD calculations, and calculating the required energy difference directly. The only disadvantage of the above strategy is that the target wave function may become spin-contaminated. We also apply a similar route, which is based on EOM-EA-CCSD calculations[10] using the ground state of NO^+ as the reference. For EOM-IP and EOM-EA we apply the core correction in

an analogous way as for the DIP calculations, computing the energy gap with the 6-311G(d,p) basis with and without the potential, and subsequently calculating the correction as a difference between the two energy gaps. The third approach is to calculate the energy difference between the $^2\Pi$ and $^1\Delta$ states by two separate calculations. In the first calculation, we use CCSD(T)[71] to compute energy of the $^2\Pi$ state of NO. Since the species is stable, no stabilization is applied. The second calculation is performed for the $^3\Sigma^-$ state of NO^- and computes the CCSD(T) energy using the NCV of 1.8 a.u. with the core correction calculated as a difference between the stabilized and unstabilized energies of the $^3\Sigma^-$ state with the 6-311G(d,p) basis.

The comparison of the CC values with other theoretical results shows a good agreement except for the two cases, i.e., EOM-IP and EOM-EA, which overestimate the value predicted by other methods by about 1 eV. Such divergence suggests that the stabilization method we use may fail when the two states of interest have a different number of electrons, which is the case for the IP and EA calculations. Note that in the case of the DIP method, which is non-particle-conserving in general, the two target states have the same number of electrons, and the agreement with other theoretical results is very good. The DIP results are within 0.2 eV or less (usually less than 0.1 eV) from the majority of other theoretical estimates. A remarkably good agreement is observed between the SF and DIP results. The discrepancy of only 0.01 eV indicates that the stabilization procedure works efficiently even in such challenging case as is the NO^- anion.

III. CONCLUSIONS

We presented the analysis and benchmarking of charge-stabilized EOM-CC calculations and introduced two corrections which account for perturbation of the target states by the stabilizing potential. The main focus was on the charge-stabilized EOM-DIP method;[23] however, charge stabilization was applied to other EOM-CC methods as well. Our benchmark set comprises CH_2, NH_2^+, SiH_2, cyclobutadiene, and NO^-.

We found that the so-called core correction based on estimating the perturbation of the target states by the stabilizing potential using auxiliary calculations in a small basis set leads to a robust computational approach. The correction greatly reduces the dependence of the excitation
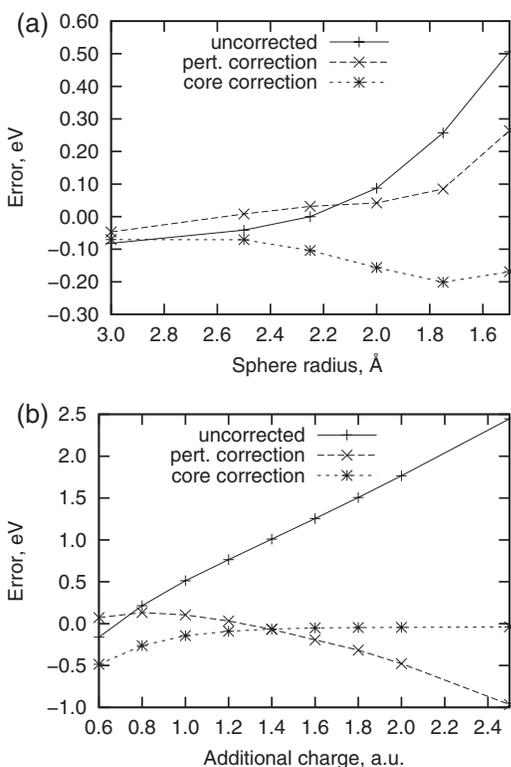

FIG. 9. DIP errors against the SF values for the adiabatic excitation energy of the ST gap of SiH_2 using the charged cage of +10 a.u. and NCV approaches, respectively. The plots show the errors of stabilized DIP for uncorrected, perturbatively corrected, and core-corrected calculations. For the core correction approach, the DIP errors and stabilization parameters corresponding to the optimal DIP accuracy (see text for details) are −0.07 eV/3.0 Å, and −0.04 eV/2.5 a.u. for the two stabilization methods, respectively.

energies on the strength of the stabilizing potential giving rise to nearly constant stabilization curves. By comparing the core-corrected stabilized DIP calculations against the SF method that does not involve stabilization, we observe the discrepancies of less than 0.28 eV, both for vertical and adiabatic excitation energies. The latter computations present a more demanding test as they involve two states at different geometries. An alternative correction based on PT was found to be less reliable.

Contrary to the conclusions based on uncorrected stabilized DIP calculations,[23] we found that the core-corrected NCV method yields better results that the charged cage method. This is encouraging because using NCV stabilization in which additional charges move with the atoms seems to be better suited for calculations of PESs than charged cage stabilization in which the stabilizing potential remains fixed.

The NO^- example illustrates the utility of the stabilization procedure beyond the DIP method. Combining the SF method and the stabilization approach, we were able to obtain the resonance energies in excellent agreement with more sophisticated calculations.

[1]M. Nooijen and R. J. Bartlett, J. Chem. Phys. **107**, 6812 (1997).
[2]M. Wladyslawski and M. Nooijen, "The photoelectron spectrum of the NO_3 radical revisited: A theoretical investigation of potential energy surfaces and conical intersections," in *ACS Symposium Series* (American Chemical Society, Washington, D.C., 2002), Vol. 828, pp. 65–92.
[3]K. W. Sattelmeyer, H. F. Schaefer, and J. F. Stanton, Chem. Phys. Lett. **378**, 42 (2003).
[4]A. I. Krylov, Annu. Rev. Phys. Chem. **59**, 433 (2008).
[5]R. J. Bartlett, Mol. Phys. **108**, 2905 (2010).
[6]K. Sneskov and O. Christiansen, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **2**, 566 (2011).
[7]R. J. Bartlett, Wiley Interdiscip. Rev.: Comput. Mol. Sci. **2**, 126 (2012).
[8]J. F. Stanton and R. J. Bartlett, J. Chem. Phys. **98**, 7029 (1993).
[9]J. F. Stanton and J. Gauss, J. Chem. Phys. **101**, 8938 (1994).
[10]M. Nooijen and R. J. Bartlett, J. Chem. Phys. **102**, 3629 (1995).
[11]A. I. Krylov, Chem. Phys. Lett. **338**, 375 (2001).
[12]S. V. Levchenko and A. I. Krylov, J. Chem. Phys. **120**, 175 (2004).
[13]A. I. Krylov, Acc. Chem. Res. **39**, 83 (2006).
[14]H. Sabbah, L. Biennier, I. A. Sims, Y. Georgievskii, S. J. Klippenstein, and I. W. M. Smith, Science **317**, 102 (2007).
[15]D. R. Yarkony, J. Phys. Chem. A **102**, 5305 (1998).
[16]L. B. Harding and A. F. Wagner, J. Phys. Chem. **90**, 2947 (1986).
[17]C. A. Taatjes, D. L. Osborn, T. M. Selby, G. Meloni, A. J. Trevitt, E. Epifanovsky, A. I. Krylov, B. Sirjean, E. Dames, and H. Wang, J. Phys. Chem. A **114**, 3355 (2010).
[18]M. Musiał, A. Perera, and R. J. Bartlett, J. Chem. Phys. **134**, 114108 (2011).
[19]M. Nooijen, Int. J. Mol. Sci. **3**, 656 (2002).
[20]L. Kong, K. R. Shamasundar, O. Demel, and M. Nooijen, J. Chem. Phys. **130**, 114101 (2009).
[21]O. Demel, K. R. Shamasundar, L. Kong, and M. Nooijen, J. Phys. Chem. A **112**, 11895 (2008).
[22]L. Kong and M. Nooijen, Int. J. Quant. Chem. **108**, 2097 (2008).
[23]T. Kuś and A. I. Krylov, J. Chem. Phys. **135**, 084109 (2011).

[24]N. Moiseyev, Phys. Rep. **302**, 211 (1998).
[25]W. P. Reinhardt, Annu. Rev. Phys. Chem. **33**, 223 (1983).
[26]N. H. Sabelli and E. A. Gislason, J. Chem. Phys. **81**, 4002 (1984).
[27]E. DeRose, E. A. Gislason, and N. H. Sabelli, J. Chem. Phys. **82**, 4577 (1985).
[28]D. D. Kharlampidi, A. I. Dementiev, and S. O. Adamson, Russian J. Phys. Chem. A **84**, 611 (2010).
[29]S. F. Izmaylov, S. O. Adamson, and A. Zaitsevskii, J. Phys. B **37**, 2321 (2004).
[30]J. S.-Y. Chao, M. F. Falcetta, and K. D. Jordan, J. Chem. Phys. **93**, 1125 (1990).
[31]B. Nestmann and S. D. Peyerimhoff, J. Phys. B: At. Mol. Phys. **18**, 615 (1985).
[32]R. McWeeny, *Methods of Molecular Quantum Mechanics*, 2nd ed. (Academic, 1992).
[33]L. V. Slipchenko, J. Phys. Chem. A **114**, 8824 (2010).
[34]M. J. Frisch, J. A. Pople, and J. S. Binkley, J. Chem. Phys. **80**, 3265 (1984).
[35]R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. **72**, 650 (1980).
[36]T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).
[37]R. A. Kendall, Jr., T. H. Dunning, and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
[38]L. V. Slipchenko and A. I. Krylov, J. Chem. Phys. **117**, 4694 (2002).
[39]Y. Shao, L. F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. Brown, A. T. B. Gilbert, L. V. Slipchenko, S. V. Levchenko, D. P. O'Neil, R. A. Distasio, R. C. Lochan, T. Wang, G. J. O. Beran, N. A. Besley, J. M. Herbert, C. Y. Lin, T. Van Voorhis, S. H. Chien, A. Sodt, R. P. Steele, V. A. Rassolov, P. Maslen, P. P. Korambath, R. D. Adamson, B. Austin, J. Baker, E. F. C. Bird, H. Daschel, R. J. Doerksen, A. Dreuw, B. D. Dunietz, A. D. Dutoi, T. R. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C.-P. Hsu, G. S. Kedziora, R. Z. Khalliulin, P. Klunziger, A. M. Lee, W. Z. Liang, I. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. M. Rhee, J. Ritchie, E. Rosta, C. D. Sherrill, A. C. Simmonett, J. E. Subotnik, H. L. Woodcock III, W. Zhang, A. T. Bell, A. K. Chakraborty, D. M. Chipman, F. J. Keil, A. Warshel, W. J. Herhe, H. F. Schaefer III, J. Kong, A. I. Krylov, P. M. W. Gill, and M. Head-Gordon, Phys. Chem. Chem. Phys. **8**, 3172 (2006).
[40]M. J. S. Dewar and G. J. Gleicher, J. Am. Chem. Soc. **87**, 3255 (1965).
[41]R. J. Buenker and S. D. Peyerimhoff, J. Chem. Phys. **48**, 354 (1968).
[42]A. Balkova and R. J. Bartlett, J. Chem. Phys. **101**, 8972 (1994).
[43]N. L. Allinger, C. Gilardeau, and L. W. Chow, Tetrahedron **24**, 2401 (1968).
[44]N. L. Allinger and J. C. Tai, Theor. Chim. Acta **12**, 29 (1968).
[45]R. C. Haddon and G. R. J. Williams, J. Am. Chem. Soc. **97**, 6582 (1975).
[46]H. Kollmar and V. Staemmler, J. Am. Chem. Soc. **99**, 3583 (1977).
[47]M. J. S. Dewar and A. Komornicki, J. Am. Chem. Soc. **99**, 6174 (1977).
[48]W. T. Borden, E. R. Davidson, and P. Hart, J. Am. Chem. Soc. **100**, 388 (1978).
[49]H. Kollmar and V. Staemmler, J. Am. Chem. Soc. **100**, 4304 (1978).
[50]J. A. Jafri and M. D. Newton, J. Am. Chem. Soc. **100**, 5012 (1978).
[51]L. J. Schaad, B. A. Hess, Jr., and C. S. Ewig, J. Am. Chem. Soc. **101**, 2281 (1979).
[52]F. Fratev, V. Monev, and R. Janoschek, Tetrahedron **38**, 2929 (1982).
[53]B. A. Hess, Jr., P. Carsky, and L. J. Schaad, J. Am. Chem. Soc. **105**, 695 (1983).
[54]H. Ågren, N. Correia, A. Flores-Riveros, and H. J. A. A. Jensen, Int. J. Quant. Chem. Symp. **19**, 237 (1986).
[55]S. S. Shaik, P. C. Hiberty, J.-M. Lefour, and G. Ohanessian, J. Am. Chem. Soc. **109**, 363 (1987).
[56]P. Carsky, R. J. Bartlett, G. Fitzgerald, J. Noga, and V. Spirko, J. Chem. Phys. **89**, 3008 (1988).
[57]K. Nakamura, Y. Osamura, and S. Iwata, Chem. Phys. **136**, 67 (1989).
[58]P. C. Hiberty, Top. Curr. Chem. **153**, 27 (1990).
[59]P. C. Hiberty, G. Ohanessian, S. S. Shaik, and J. P. Flament, Pure Appl. Chem. **65**, 35 (1993).
[60]Y. Mo, W. Wu, and Q. Zhang, J. Phys. Chem. **98**, 10048 (1994).
[61]M. N. Glukhovtsev, S. Laiter, and A. Pross, J. Phys. Chem. **99**, 6828 (1995).
[62]R. L. Redington, J. Chem. Phys. **109**, 10781 (1998).
[63]J. C. Sancho-Garcia, J. Pittner, and P. Carsky, J. Chem. Phys. **112**, 8785 (2000).
[64]J. C. Sancho-Garcia, A. J. Perez-Jimenez, and F. Moscardo, Chem. Phys. Lett. **317**, 245 (2000).
[65]F. Koike, J. Phys. Soc. Jpn. **39**, 1590 (1975).
[66]D. Teillet-Billy and F. Fiquet-Fayard, J. Phys. B **10**, L111 (1977).
[67]J. Tennyson and C. J. Noble, J. Phys. B **19**, 4025 (1986).

[68] F. J. da Paixao, M. A. P. Lima, and V. McKoy, Phys. Rev. A **53**, 1400 (1996).

[69] Z. Zhang, W. Vanroose, C. W. McCurdy, A. E. Orel, and T. N. Rescigno, Phys. Rev. A **69**, 062711 (2004).

[70] C. S. Trevisan, K. Houfek, Z. Zhang, A. E. Orel, C. W. McCurdy, and T. N. Rescigno, Phys. Rev. A **71**, 052714 (2005).

[71] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).